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Request for grant of a patent

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1. Your reference P18142/HGR/BOU

31 MAY 1997

Patent application number
(The Patent Office will fill in this part)

9711178.5

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Giltech Limited
9/12 North Harbour Industrial Estate
AYR
KA8 8AA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

401582202

4. Title of the invention

"Method"

5. Name of your agent (if you have one)

Murgitroyd & Company

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

373 Scotland Street
GLASGOW
G5 8QA

Patents ADP number (if you know it) 1198013

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Yes

Patents Form 1/77

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Description	9
Claim(s)	0
Abstract	0
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Priority documents	-
Translations of priority documents	-
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	-
Request for preliminary examination and search (Patents Form 9/77)	-
Request for substantive examination (Patents Form 10/77)	-
Any other documents (please specify)	-

11.

I/We request the grant of a patent on the basis of this application.

Signature *Murgitroyd & Co*
Murgitroyd & Company

Date
30 May 1997

12. Name and daytime telephone number of person to contact in the United Kingdom

Beverley Ouzman
0141 307 8400

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1 **METHOD**

2

3 The present invention relates to a method for the
4 production of water soluble glass fibres and glass
5 wool.

6

7 It is known that certain glasses, in which the usual
8 glass former, silicon dioxide, is replaced with
9 phosphorous pentoxide, are soluble in water and body
10 fluids. The rate of dissolution is controlled largely
11 by the addition of glass modifiers such as calcium
12 oxide. In simple terms, the greater the concentration
13 of the modifier the slower the rate of dissolution.
14 The rate of dissolution may range from minutes through
15 to several years.

16

17 Soluble phosphate based glasses which have demonstrated
18 good biocompatibility can incorporate inorganic metals

19 such that a sustained release of the metals can be
20 provided at the wound site. Such materials can also
21 find use in mechanical applications where, for example,
22 slow release of an anti-corrosion agent may be
23 beneficial.

24

25 Certain applications require that the glass is in the

1 form of wool or fibres for mechanical applications such
2 as insulation wool and packaging. Thus, for example,
3 Mohr et al in "Fiber Glass" (Van Norstrand, Reinhold
4 Company, New York 1978) and Jaray in "A New Method of
5 Spinning Glass Fibers" (28th Annual SPI RP/C Institute
6 proceedings 1973, Section 3-A) describe the production
7 of wool and fibres, respectively, from molten glass.
8 The glass fibres can be used for insulation,
9 construction or even communication purposes. Glass
10 wool also finds uses in packaging and insulation
11 applications.

12
13 Normally, glass fibres are produced from molten glass
14 using traditional fibre pulling techniques; whereby
15 filaments of high temperature molten glass (850°-
16 1300°C) are formed into strands and stretched over pull
17 rolls before being collected onto a reel.

18
19 Glass wool formation is similar in that the glass is
20 initially melted in a crucible. The crucible has
21 suitable apertures to allow filaments of glass to flow
22 downwards, which are then "blown" into wool using jets
23 of either steam or compressed air. Alternatively,
24 glass wool can be formed using a flame attenuation
25 process, developed by Owens-Corning Fiberglas
26 Corporation circa 1940. In this process molten glass
27 passes through a bushing stage where primary filaments
28 approximately 1 mm wide are formed. The fibres are

29 then aligned into an exact uniformly juxtaposed array,
30 using a fibre guide, into a jet flame issuing from an
31 internal combustion burner. The jet flame causes
32 thinning and lengthening of the fibres before they are
33 collected on a steel mesh belt.

34
35 In both cases, the glass is either supplied in molten
36 form direct from a crucible or from a temperature-

1 gradient furnace.

2

3 Generally, water soluble glasses do not lend themselves
4 to these traditional fibre and wool forming techniques.

5 As an example, US Patent 4,604,097 of Graves et al
6 discloses a water soluble drawn fibre, composed
7 primarily of calcium oxide and phosphorous pentoxide.

8 The fibre produced has a very low tensile strength,
9 compared to fibres spun from non-soluble glass
10 compositions.

11

12 Further, water soluble glasses can also be chemically
13 aggressive when molten, unlike traditional glasses
14 where silicon dioxide is used as the glass former.
15 Additionally, the fibres produced are prone to thermal
16 shock and can suffer from devitrification or
17 crystallisation.

18

19 To combat problems of devitrification and
20 crystallisation, water soluble glass fibres have been
21 previously produced in exacting conditions. Thus, for
22 example, Zimmer et al in WO92/07801 discloses drawing
23 fibres from a water soluble glass composed primarily of
24 phosphorus pentoxide, calcium oxide and iron oxide. In
25 order to keep the viscosity of the glass suitable for
26 drawing, the fibres were drawn at 1200°C. Also as a
27 result of the chemically aggressive nature of the glass
28 at that temperature the glass was pulled in an oxygen

29 rich atmosphere (as high as 80% oxygen by volume).

30 Obviously the commercial production of glass fibres
31 under these high temperature controlled atmospheric
32 conditions is expensive.

33

34 The problems of working with water soluble glass are
35 compounded by the very nature of the glass. Metal
36 oxides of elements such as lead and tellurium have

1 previously been used in glass as additives to affect
2 qualities of the glass; crystallisation temperature,
3 viscosity and density, for example. As a result of
4 environmental concerns and particularly when the
5 glasses are to be used in a biological application
6 these additives must be avoided and replaced by more
7 acceptable alternatives.

8
9 Therefore, it is an object of the present invention to
10 provide environmentally acceptable water soluble glass
11 fibres with suitable mechanical properties, and to
12 produce said fibres under less forcing conditions.

13
14 The present invention provides a method for forming
15 glass fibre and/or glass wool, the method comprising
16 producing molten glass, allowing at least a portion of
17 said molten glass to cool to a working temperature and
18 then processing to form fibres and/or wool therefrom.

19
20 The glass is preferably a water soluble glass.

21
22 Generally, the glass is initially heated to a melting
23 temperature of 700°-1150°C, preferably 750°-1050°C.

24
25 Generally, the working temperature of the glass will be
26 at least 200°C lower than the melting temperature.
27 Suitable working temperatures may fall within the range
28 500°-900°C, preferably 550°-700°C, more preferably

29 550°-650°C, especially 600°-650°C. Depending upon the
30 glass composition used, the working temperature may
31 have a range of only 10°C, so that fibre formation may
32 occur only between the temperature of $N-(N+10)^{\circ}\text{C}$.

33 Other glass compositions may have a wider temperature
34 range in which glass formation is possible.

35
36 Alternatively, the working temperature of the glass may

1 be defined as 100-300°C above the Tg of the glass.

2

3 With reference to the "working temperature" of the
4 glass, the skilled person will appreciate that the
5 furnace temperature may differ considerably from the
6 temperature of the glass itself and indeed there may be
7 a significant temperature gradient in the glass.

8 Ideally the "working temperature" will be the

9 temperature of the glass as fibre formation (ie.

10 pulling) takes place. In many compositions however, it

11 may not be practical to measure the temperature at the

12 surface of the glass where pulling occurs by insertion

13 of a temperature probe as the introduction of the probe

14 may precipitate crystallisation of the glass. One

15 alternative is to place a temperature probe into the

16 bushing and to monitor the bushing temperature which

17 will be a good indicator of the glass temperature at

18 the moment of fibre formation. Alternatively an Infra

19 Red pyrometer may be focused onto the appropriate area

20 of the glass and used to monitor the temperature.

21

22 The glass to be formed into fibres will generally be

23 heated until molten and cooled slowly until the

24 appropriate working temperature is reached and fibre

25 formation can commence. The initial heating of the

26 glass above its melting point and the subsequent fibre

27 formation may be carried out in a single vessel or,

28 alternatively, the molten glass may be transferred to a

29 vessel designed specifically for fibre formation. One

30 way of holding the molten glass in a vessel having a

31 bushing within its lower surface until the temperature

32 drops to the required working temperature is to coat or

33 fill the holes of the bushing with a material that

34 gradually melts over the period of time taken for the

35 glass to reach the temperature required.

36

1 According to a further aspect of the present invention
2 there is provided a composition suitable for processing
3 into glass fibres and/or wool.

4
5 Phosphorous pentoxide (P_2O_5) is preferably used as the
6 glass former.

7
8 Generally the mole percentage of phosphorous pentoxide
9 in the glass composition is less than 85%, preferably
10 less than 60% and especially between 30-60%.

11
12 Alkali metals, alkaline earth metals and lanthanoid
13 oxides or carbonates are preferably used as glass
14 modifiers.

15
16 Generally, the mole percentage of alkali metals,
17 alkaline earth metals and lanthanoid oxides or
18 carbonates is less than 60%, preferably between 40-60%.

19
20 Boron containing compounds are preferably used as glass
21 additives.

22
23 Generally, the mole percentage of boron containing
24 compounds is less than 15%, preferably less than 5%.

25
26 Other compounds may also be added to the glass to
27 modify its properties, for example SiO_2 , Al_2O_3 , SO_3 or
28 transition metal compounds (eg. first row transition

29 metal compounds).

30
31 Generally, the mole percentage of these additives in
32 the glass is less than 25%, preferably less than 10%.

33
34 Embodiments of the invention will be described with
35 reference to the following non-limiting examples.

1 **Example 1**

2		Component	Mole %
3	Glass Composition		
4		Na ₂ O	31.05
5		CaO	16.00
6		Ag ₂ O	3.88
7		P ₂ O ₅	46.08
8		Na ₂ PO ₃ F	0.97
9		2Al ₂ O ₃ .B ₂ O ₃	2.00

10

11 100 grams of the sample was heated to 900°C before
 12 being cooled and pulled at 650°C, at 25 km/hr. Overall
 13 the fibre was good; one sample was 10 km in length and
 14 11 grams in weight, although there was some
 15 crystallisation at the pulling temperature.

16

17 **Example 2**

18		Component	Mole %
19	Glass Composition		
20		Na ₂ O	29.51
21		CaO	15.21
22		Ag ₂ O	3.68
23		P ₂ O ₅	43.80
24		2Al ₂ O ₃ .B ₂ O ₃	1.90
25		Na ₂ PO ₃ F	1.90
26		Na ₂ B ₄ O ₇ .10H ₂ O	1.00
27		Na ₂ PO ₄	3.00

28

29 74 grams of the sample was heated to 1000°C before
 30 being cooled and pulled at 635°C at 25 km/hr. The
 31 fibre produced was ultrafine; one sample was 18 km in
 32 length and 59 grams in weight. The sample was sprayed
 33 with WD40 to prevent water absorption and to aid
 34 lubricity. There was some debris at the bottom of the
 35 crucible, but this was found to be just iron deposits
 36 from the brushing rod.

1 **Example 3**

2

3

4 Glass Composition

5

6

7

8

9

10 200 grams of the sample was heated to 1050°C before
11 being cooled and pulled at 635°C at 25 km/hr. The
12 fibre was good although there was some crystallisation
13 at the pulling temperature.

14

15 **Example 4**

16

17

18 Glass Composition

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20

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26 117 grams of the sample was heated to 950°C before
27 being cooled and pulled at 635°C, at 40 km/hr. The
28 fibre produced was good and there were no

29 crystallisation problems even though the surface
30 temperature of the fibre dropped to 510°C in the
31 pulling process.

32

33

34

35

36

1 **Example 5**

2
3
4 **Glass Composition**

Component	Mole %
Na ₂ O	31.71
CaO	14.73
P ₂ O ₅	36.33
B ₂ O ₃	4.78
SO ₃	9.40
Na ₂ PO ₃ F	3.00

5
6
7
8
9
10
11
12 99 grams of the sample was heated to 800°C before being
13 cooled to 650°C and pulled at 40 km/hr. The fibre
14 produced was very fine but difficult to pull and quite
15 fragile at speed.

16
17 **Example 6**

18
19
20
21 **Glass Composition**

Component	Mole %
Na ₂ O	30.77
CaO	14.28
P ₂ O ₅	35.28
B ₂ O ₃	4.64
SO ₃	9.12
FePO ₄	2.41
Wa ₂ PO ₃ F	0.20
Na ₂ PO ₃ F	0.20
MnHPO ₄	2.06

22
23
24
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26
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28
29
30
31
32 200 grams of the sample was heated to 850°C before
33 being cooled to 545°C and pulled at 40 km/hr. The
34 fibre produced was strong and thin; there was not a
35 problem of crystallisation, in fact the glass can be
36 stored at 550°C for 72 hours without the onset of
37 crystallisation.

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